



Influence of alkali catalysts on the production of hydrogen-rich gas from the hydrothermal gasification of food processing waste

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ABSTRACT

Sub-critical water gasification by partial oxidation of glucose was carried out in the presence of various alkali catalysts; NaOH, KOH, $\text{Ca}(\text{OH})_2$, Na_2CO_3 , K_2CO_3 and NaHCO_3 . Experiments were carried out in a closed batch reactor under sub-critical water conditions of 330 °C temperature and 13.5 MPa pressure. Hydrogen gas yield in relation to the alkali catalyst was in the following order; $\text{NaOH} > \text{KOH} > \text{Ca}(\text{OH})_2 > \text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{NaHCO}_3$. The metal hydroxides produced higher H_2 gas yield than the carbonates or bicarbonate. Carbon dioxide was the predominant gas product in the presence of metal carbonate and bicarbonates. Catalysts of the hydroxide ion group, NaOH, KOH and $\text{Ca}(\text{OH})_2$, were selected to react with representative food processing wastes in the form of molasses and rice bran under hydrothermal condition. The results indicated that NaOH, KOH and $\text{Ca}(\text{OH})_2$ could promote biomass decomposition and improve the amount of H_2 product via the water-gas shift reaction by intermediate formation of formate salts. In addition, NaOH, KOH and $\text{Ca}(\text{OH})_2$ inhibited and suppressed tar and char formation. NaOH was also effective in capturing the CO_2 formed, thereby shifting the water-gas shift reaction equilibrium in the forward direction. In addition, results showed that hydrothermal gasification at low temperature depended not only on the metal ion (Na^+ , K^+ and Ca^{2+}) but also on their species and concentrations. It is suggested that the basicity strengths of the aqueous solutions of alkali additives may have enhanced the initial decomposition of biomass into gasifiable intermediates, especially during the heat-up period.

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1. Introduction

Most commonly used biomass such as food processing wastes [1,2] and various biomass-derived feedstocks [3,4] contain various complex compositions that typically consist of carbohydrates, proteins and oils and fats [5]. To simplify the hydrothermal gasification, many researchers have utilized model compounds, for instance, cellulose, glucose, xylan, glycerol, p-cresol, and phenol, to simulate the behaviour of real biomass for hydrogen production [6]. More recently, Matsumura et al. [7] investigated and reported the kinetics of glucose decomposition and also Williams and Onwudili [8] reported the composition of both the gas and bio-oil products obtained from partial oxidative gasification of glucose under sub-critical water conditions.

Many researchers have used catalysts in both sub-critical and supercritical water (hydrothermal) gasification of biomass, to influence gas formation. Furthermore, some catalysts can play a major role in influencing the types of biomass decomposition that are important for hydrogen or syngas production [9]. Addition of

certain catalysts primarily reduces and suppresses char and tar formation at low operating temperatures [9,10]. Minowa and co-workers studied biomass gasification with nickel catalyst and sodium carbonate in hot-compressed water at temperature around 400 °C and pressure of 20 MPa [11,12]. They found that nickel catalyst reduced the amounts of chars and tars.

Alkaline homogeneous catalysts/additives such as KOH, NaOH, K_2CO_3 , and Na_2CO_3 have gained prominence because they can dissolve in the hydrothermal medium as well as promote biomass gasification [13]. Additionally, alkaline additives increase gasification efficiency and higher hydrogen yield by accelerating the water-gas shift reaction via the formation of formate salts [4,14–20]. Sinag et al. [18,19] gasified glucose under supercritical water gasification with addition of K_2CO_3 and reported increased hydrogen gas production. Kruse et al. [20] investigated gasification of pyrocatechol used as a model compound for lignin in biomass and for aromatic compounds in wastewaters carried out under supercritical water in the presence of KOH. They found that the composition of gas products changed in favour of hydrogen gas in the presence of the alkali. Moreover, Schmieder et al. [21] found that the addition of KOH or K_2CO_3 during the gasification of glucose and glycine at 600 °C and 25 MPa gave a hydrogen-rich gas product with CO_2 as the main carbon compound. Xu et al. [22] used

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Table 1

Proximate and ultimate compositions of model compound and food waste samples.

Sample	Moisture content	Proximate analysis ^a			Ultimate analysis ^a			
		Volatile matter	Fixed carbon	Ash	C	H	N	O ^b
Glucose	–	87.1	12.9	–	40.4	7.20	–	52.2
Molasses	30.0	94.2	1.45	4.32	30.9	6.67	0.85	61.6
Rice bran	10.8	82.9	7.10	10.0	44.4	7.11	2.16	46.3

^a Weight percent on dry basis.^b By difference.

glycine and glycerol as the model compounds of protein and fat respectively for the gasification process operated at 380–500 °C and 25 MPa with or without Na₂CO₃ catalyst. They found that Na₂CO₃ catalyst increased hydrogen yield. Their reports showed that super-critical water gasification was feasible for converting biomass or organic pollution matter containing protein or fats to hydrogen gas.

In this work, the effects of several alkaline additives (NaOH, KOH, Ca(OH)₂, Na₂CO₃, K₂CO₃ and NaHCO₃) for partial oxidative gasification of biomass in sub-critical water have been investigated. These screening experiments were conducted at moderately low temperature compared to those found in the literature for hydrothermal biomass gasification [20–22] for the production of hydrogen gas. While other researchers have shown that alkali compounds were effective for hydrothermal biomass conversions, most of these reports were based largely on the production of bio-oils [23–25]. Earlier investigations showed that NaOH used as an additive, could promote biomass gasification in two main ways; by decomposing the biomass to gasifiable intermediates such as formate and acetate; and the promotion of water-gas shift reaction by the capture of CO₂ to form sodium carbonate/bicarbonate [17]. Literature has confirmed that in the presence of sodium hydroxide oil or tar formation was suppressed. However, it is not clear if the positive effect of the alkali on biomass gasification is due to the metal ions, hydroxide ions or both. In order to test this hypothesis, this work investigated a selection of hydroxides, carbonates and bicarbonate of sodium, potassium and calcium.

Experiments involved the reaction of real food processing wastes (molasses, glucose and rice bran) at reaction temperature of 330 °C and autogenic pressure of 13.5 MPa. This temperature was sufficiently high to degrade the structure of these samples to produce gasifiable intermediates by the action of sodium hydroxide for H₂ production [26]. The screening of the additives was carried out with glucose, being a widely used biomass model compound in the research literature. Our earlier paper [17] has shown that cellulose, starch, rice husk, potato and rice straw could all be converted to hydrogen and methane at 450 °C, 31 MPa in the presence of NaOH. Moreover, glucose has also been the choice of most research reports in literature, with sufficient data for comparison. Molasses and rice bran were selected as by-products of sugar cane manufacturing and rice milling processes, respectively. While molasses is composed mainly of sugar-type compounds [27,28], rice bran is composed of fibre or hemicelluloses, proteins and oil. Both molasses and rice may therefore be regarded as potential renewable energy resources for hydrogen generation because they are cheap and widely abundant [28,29].

2. Experimental

2.1. Raw materials and reagents

Hydrogen peroxide (30%, w/v), potassium hydroxide, potassium carbonate, sodium carbonate and sodium bicarbonate were all purchased from Sigma–Aldrich, UK, while sodium hydroxide pellets (Analar Normapur) were obtained from VWR International Ltd, UK. Glucose was supplied by Alfal Aeser, UK and calcium hydroxide

from Rose Chemical Limited, UK. By-products from food processing industry such as molasses and rice bran were obtained as real-world biomass samples and characterised as presented in Table 1.

The proximate (volatile matter fixed carbon and ash) analysis of the glucose, molasses and rice bran biomass/food processing waste samples were determined using a Shimadzu TGA 50 thermogravimetric analyzer. The sample was heated to 800 °C at 25 °C min^{−1} in nitrogen where pyrolysis occurred followed by introduction of air for combustion of the residual char, leaving a residual ash. Elemental (ultimate) analysis was performed with a CE Instruments Flash EA 1112 Elemental Analyzer.

From Table 1, the mole ratio of C:H:O in glucose as carbohydrates model compound is approximately 1:2:1, while the mole ratio of carbon:hydrogen:oxygen in molasses and rice bran we found experimentally to be 0.77:2:1.15 and 1.04:2:0.81, respectively. Even though molasses and rice bran have C:H:O ratios slightly different from glucose, we have previously shown that irrespective of the ratio and type of bond linkages present in the biomass, sodium hydroxide was able to produce hydrogen and methane gases at identical proportions. For instance, glucose and cellulose with different bond linkages were equally decomposed to produce mainly hydrogen and methane [17]. Our argument has been that alkalis are able to decompose various types of carbonaceous materials including components of biomass such as cellulose, hemi-cellulose and lignin, to gasifiable intermediates, which produce mainly hydrogen and methane at higher temperature [17,26].

2.2. Reactor system and experimental procedure

Hydrothermal gasification of glucose, molasses and rice bran was investigated in a Hastelloy C reactor obtained from the Parr Instrument Co., Moline, IL, USA and the reactor has a 75 ml of volume capacity and a maximum operating temperature and pressure of 600 °C and 45 MPa, respectively. The temperature of the system was monitored with the aid of a thermocouple inserted in a thermowell located at the bottom of the reactor which extends to the interior of the vessel. Pressure was monitored directly by means of a pressure gauge fitted to the top of the reactor. At the head of the reactor is fitted a gas sampling tube with two high-pressure valves. This is used for gas sampling at the end of the reaction. Also the batch reactor has been described in earlier published papers [17,26,30]. In each experiment, a total liquid volume of 15 ml was used and a known amount of sample (glucose, molasses and rice bran solution) was loaded into the reactor, which was then placed in ceramic heater obtained from Carbolite, UK and heated at a rate of 12 °C min^{−1} to the designated temperature. The 15 ml liquid was made up of deionised water and 0.75 ml of a 30% (w/w) hydrogen peroxide, representing an oxidant equivalence ratio of 0.28, calculated based on the work of Jin et al. [31]. Each experiment was held at 330 °C for 60 or 120 min. Evidence from our earlier work shows that the maximum hydrogen gas yield was achieved after 120 min of reaction. However, the increase in the gas yield between 60 min and 120 min was minimal and on the basis of that we reaction time in the range of 60 and 120 min to determine H₂ production from by-products of food industry in the presence of the alkali additives.

Since the reactor was a closed system, the reaction pressure depended on the reaction temperature and water loading in the reactor. With 15 ml liquid (mainly water) loading the pressure was 13.5 MPa at 330 °C. After each experiment, the reactor removed from the heater and rapidly cooled to room temperature by an air cooling system. Using this system, the reactor temperature drops rapidly from 330 °C to less than 200 °C in under 10 min and to less than 100 °C under 30 min. However, it takes up to 90 min for the reactor to completely reach ambient temperature (20 °C). Since both heating up and cooling processes were identical for all experiments, the effects of these would likely be similar to all the reactions considered.

2.3. Products analysis

2.3.1. Gas analysis

After cooling to ambient temperature, the internal pressure of the reactor caused by the presence of produced gases was noted along with the temperature reading. The gas sampling valve was the opened to release the gas into a gas-tight plastic syringe, which was then covered with a gas-tight rubber stopper. The gas products were analysed on standalone gas chromatographs immediately after sampling. The gas sample was analysed by injection into two separate gas chromatographs to measure the vol% of the components of gas samples namely, H₂, CO, CO₂, CH₄, and C₂–C₄. A Varian CP-3380 gas chromatograph with a thermal conductivity detector (GC/TCD) and fitted with two columns was used. A 2 m long × 2 mm diameter, 60–80 mesh packed molecular sieve column was used to separate hydrogen, oxygen, nitrogen, and carbon monoxide while a packed Haysep column of similar dimensions was used for analysing carbon dioxide. Argon was used as the carrier gas. The column oven was held isothermally at 40 °C for the analysis and the injector oven was at 120 °C. The detector temperature was 120 °C with a filament temperature of 160 °C.

Hydrocarbon gases from C₁ to C₄ were analysed using a second Varian CP-3380 gas chromatograph with flame ionisation detector (GC/FID). The column used is 2 m long × 2 mm diameter and packed with 80–100 mesh Haysep. The injector was held at 150 °C; while the detector temperature was 200 °C. Nitrogen was used as the carrier gas. The oven temperature programme was 60 °C for 3 min, with a heating rate of 10 °C min^{−1} to 100 °C, held for 3 min, finally ramped to 120 °C at 20 °C min^{−1}, and held for 9 min at 120 °C. On the basis of the vol% obtained from the GCs, volume occupied by the gas, Henry's law, ambient temperature and final pressure of the cooled reactor (5–10 bar), the mass of each gas component could be calculated using the general gas law.

For glucose, molasses and rice bran, the proportion of each gas product was calculated as:

$$\text{yield (g of gases/kg of sample)} = \frac{\text{gram of each gas produced}}{\text{kg of sample}} \times 100 \quad (1)$$

2.3.2. Liquid and solid analysis

Liquid sample and solid residue consisting of tar, char, and aqueous effluents were obtained from the reactor after the sub-critical water gasification process. The liquid effluent obtained from each experiment was poured out into a clean reagent bottle. The reactor was rinsed with deionized water until the rinsed liquid was clear and added to the bottle. The total volume of this aqueous phase was noted. The colour of the homogenous liquid effluents ranged from brown to almost clear depending on the additive used. The liquid effluent from the reactor contained total water-soluble products (TWSP), which was expected to be a mixture of organic

and inorganic compounds. Where tar formation was observed, the tar was mostly usually found on the walls of the reactor, with a few droplets in the liquid effluent. The liquid sample was homogenized thoroughly in the reagent bottle and 50 ml transferred into separating funnel and ethyl acetate was added to separate the ethyl acetate-extractable compounds by liquid–liquid extraction. Earlier, we have found that adding ethyl acetate to strongly alkaline liquid effluents led to the formation of more sodium acetate, thereby giving large overages in mass balance calculations [32]. Usually, if char was produced, it would be partitioned into the ethyl acetate layer and this was separated by filtration. The filtered organic phase containing the tar was transferred into a bottle. Additional ethyl acetate was added to the reactor to rinse out the tar still remaining in the reactor. This organic phase/tar was added to the ethyl acetate extract. This ethyl acetate extract (organic phase) was quantitatively collected and evaporated with a gentle stream of nitrogen gas, placed in a desiccator to dry off the moisture overnight, and then weighed to determine the total mass of oil/tar produced. The mass of the total water-soluble products in the liquid effluent straight from the reactor was determined by transferring another 50 ml aliquot of aqueous phase from the reagent bottle into a crucible, weighed and placed on a water bath to evaporate off the water. After evaporating the water, the sample was dried in the crucible at 105 °C to a constant weight to determine the mass of total water-soluble products. In all cases involving the addition of alkaline compounds, the amount of solid residue (TWSP) was significantly higher than the amount of tar. For instance, while the tars weighed an average of 100 mg, the solid residues weighed up to 1800 mg, indicating much higher contribution of the non-ethyl acetate-extractable components (e.g. dissolved inorganic compounds) to the weight of the total water-soluble products obtained.

Furthermore, the total residue carbon (TC) containing total organic carbon (TOC) and inorganic carbon (IC) content in the liquid effluent was determined by an IL550 TOC-TN analyzer (Hach-Lange Co., UK). The description and operation of the TOC analyzer have been given in earlier paper [26]. The yield of TOC and TIC in the liquid effluents was defined by Eqs. (2) and (3) based on gram of total carbon in sample.

$$\begin{aligned} \text{TOC yield (mol-organic carbon/mol-C in sample)} \\ = \frac{\text{moles of organic carbon in aqueous phase}}{\text{moles of carbon atom in sample}} \times 100 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{TIC yield (mol-inorganic carbon/mol-C in sample)} \\ = \frac{\text{moles of inorganic carbon in aqueous phase}}{\text{moles of carbon atom in sample}} \times 100 \end{aligned} \quad (3)$$

These equations were adapted from Stander and Theodore's Environmental Regulatory Calculations Handbook [33].

The dried solid residues obtained after evaporation of the aqueous phase were scanned on an X-ray diffractometer via a Phillips PW1050 Goniometer with a Philips PW1730 generator and CuKα radiation tube. The XRD identified the crystalline substances present in the solid residue. The sample was finely ground to less than 75 μm size and mounted on a 20 mm aperture of an aluminium sample holder. The instrument was equipped with Hiltonbrooks' HBX data acquisition software to collect the data. GBC Scientific Equipment Ltd's TRACES software using ICDD PDF2 (International Centre for Diffraction Data Powder Diffraction Files) database was used for phase identification.

The amount of water produced from the decomposition of hydrogen peroxide to water and oxygen was calculated theoretically. The total mass balance was based on the total mass of the reactants (feed), including the model compound, NaOH, and hydro-

gen peroxide used:

$$\text{percentage mass balance} = \frac{\text{summation of mass products}}{\text{summation of reactants}} \times 100 \quad (4)$$

The reactants in Eq. (4) include organic sample, H₂O₂ and alkali additives.

The product char and oil/tar were analysed for carbon, hydrogen, nitrogen, and oxygen contents using a Carlo Erba Flash EA 1112 compact analyzer. Automated determination of CHNS in one sample and oxygen in another sample was carried out. Between 2.5 and 3.5 mg of the char was used for each analysis. The elemental analysis of the oil and char was used in the calculation of the carbon and hydrogen mass balances.

Percentage carbon mass balance was calculated using the results obtained for each carbon-containing product as follows;

$$\frac{\text{summation of carbon amount in each product}}{\text{total carbon amount in reactants}} \times 100 \quad (5)$$

Percentage hydrogen mass balance was calculated using the results obtained for each hydrogen-containing product as follows:

$$\frac{\text{summation of hydrogen amount in each product}}{\text{total hydrogen amount in reactants}} \times 100 \quad (6)$$

3. Results and discussion

Low temperature processes favour energy savings, hence this study investigated hydrogen gas production via alkaline hydrothermal gasification of biomass samples at a relatively low temperature of 330 °C compared to the works of others [20–22]. The reactions were carried out in the presence of hydroxide additives (NaOH, KOH, Ca(OH)₂, carbonates (Na₂CO₃, K₂CO₃) and bicarbonate (NaHCO₃). In our earlier work, we observed the catalytic biomass decomposition by NaOH at temperatures around 200 °C to form dark-brown coloured water-soluble products [17]. This part of the study investigated the effect of these alkaline additives on hydrogen production from glucose, which has been used extensively as biomass model compound.

3.1. Sub-critical water gasification of glucose with alkaline additives

A study of the effect of various alkali catalysts on the gasification of glucose was investigated at reaction temperature and reaction time of 330 °C and 120 min, respectively. Under alkaline hydrothermal condition, each experiment involved 0.75 g of glucose reacting in the presence of 1 g of each additive (nominal concentration; 6.67%, w/v) in 15 ml mixture of deionized water and H₂O₂. This study was undertaken in order to firstly compare the effect of equivalent amount of the additive. To do this in as simple a manner as possible, this report will focus on gas products and particularly H₂ gas as the target product. However, the results of reaction of glucose under sub-critical water gasification and total mass balance in the presence of various catalysts (1 g each) at 330 °C for 120 min of reaction time and 0.28 equivalent ratio of H₂O₂ each are shown in Table 2. Reactions involving sodium and potassium additives resulted in soluble aqueous products which consisted mainly of carbonates and some metal salts of acetic acid and formic acids. In Tables 3 and 4, it can be seen that carbon and hydrogen recoveries were in all cases more than 84% and 81.4%, respectively. These recovery values indicate possible loss of volatile organic compounds during analysis.

Fig. 1 is a plot of gas yields versus different additives used. The yield of gas products was defined as gram of gases per kilogram of glucose sample. From Fig. 1, it

Table 2
Total mass balance of products in relation to reaction conditions during glucose gasification with various catalysts at 330 °C and 120 min of reaction time.

Reaction condition	H ₂ O ₂ (ER)	Catalysts (%w/v)	H ₂ (mg)	CO (mg)	CO ₂ (mg)	C ₁ –C ₄ (mg)	Oil/tar (mg)	Solid residues/char (mg)	TWSP ^a (mg)	H ₂ O (mg)	% mass balance
NaOH	0.28	6.67	19.7	–	–	2.20	–	–	1800	296	107
KOH	0.28	6.67	15.9	0.40	45.2	2.21	71.0	–	1630	263	103
Ca(OH) ₂	0.28	6.67	7.20	9.00	3.00	2.51	–	1110 ^b	105	535	89.7
Na ₂ CO ₃	0.28	6.67	6.40	1.00	210	1.90	84.0	–	1330	205	92.8
K ₂ CO ₃	0.28	6.67	6.90	0.70	182	2.13	101	–	1480	194	99.6
NaHCO ₃	0.28	6.67	3.10	1.10	300	2.10	127	–	1030	270	87.7

ER = oxidant equivalence ratio.

^a TWSP = total water-soluble product containing both organic and inorganic compounds.

^b Solid residue included calcium carbonate.

Table 3

Carbon mass balance of products in relation to reaction conditions during glucose gasification with various catalysts at 330 °C and 120 min of reaction time.

Reaction condition	H ₂ O ₂ (ER)	Catalysts (%w/v)	CO (mg)	CO ₂ (mg)	C ₁ –C ₄ (mg)	Oil/tar (mg)	Solid residues/char (mg)	TWSP ^a (mg)	% mass balance
NaOH	0.28	6.67	–	–	1.8	–	–	270	90.5
KOH	0.28	6.67	0.21	12.3	1.82	–	–	253	89.1
Ca(OH) ₂	0.28	6.67	3.80	0.80	2.10	–	133	131	90.2
Na ₂ CO ₃	0.28	6.67	0.41	57.3	1.61	46.2	–	264	89.4
K ₂ CO ₃	0.28	6.67	0.33	49.7	1.71	76.8	–	197	84.0
NaHCO ₃	0.28	6.67	0.52	81.8	1.71	93.0	–	226	90.9

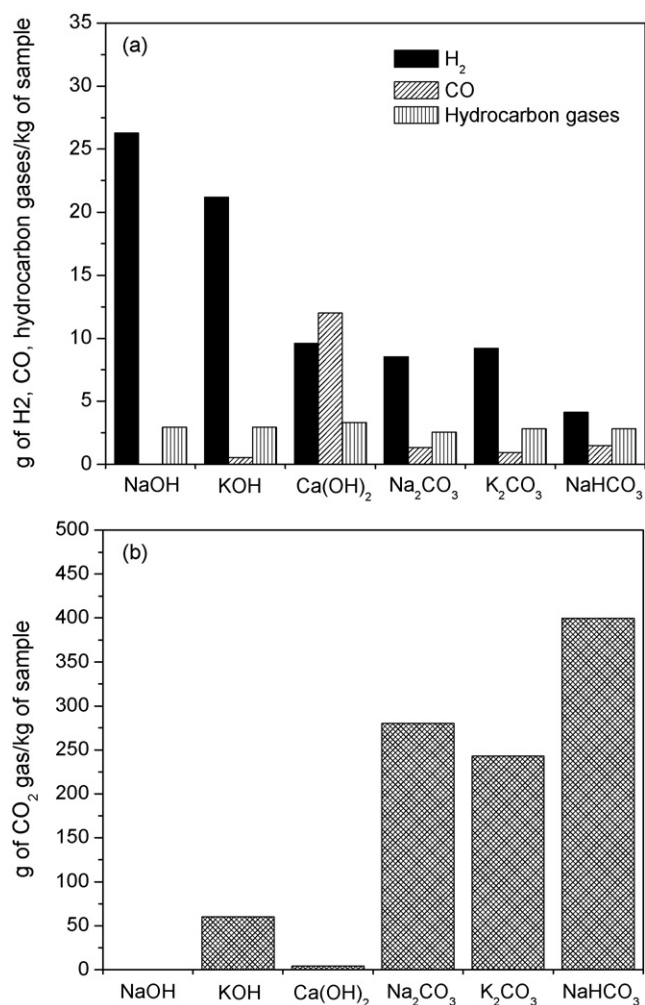
ER = oxidant equivalence ratio.

^a Total water soluble products including organic and inorganic compounds.**Table 4**

Hydrogen mass balance of products in relation to reaction conditions during glucose gasification with various catalysts at 330 °C and 120 min of reaction time.

Reaction condition	H ₂ O ₂ (ER)	Catalysts (%w/v)	H ₂ (mg)	C ₁ –C ₄ (mg)	Oil/tar (mg)	Solid residues/char (mg)	TWSP ^a (mg)	H ₂ O (mg)	% mass balance
NaOH	0.28	6.67	19.7	0.50	–	–	24.1	32.9	87.0
KOH	0.28	6.67	15.9	0.40	–	–	37.7	29.2	102
Ca(OH) ₂	0.28	6.67	7.20	0.43	–	–	6.75	59.5	81.4
Na ₂ CO ₃	0.28	6.67	6.40	0.40	4.62	–	17.2	22.8	81.4
K ₂ CO ₃	0.28	6.67	6.90	0.40	7.20	–	32.3	21.6	108
NaHCO ₃	0.28	6.67	3.10	0.45	8.24	–	20.4	30.0	82.2

ER = oxidant equivalence ratio.

^a Total water soluble products including organic and inorganic compounds.**Fig. 1.** Yields of gas products from glucose gasification in relation to type of alkaline additive: (a) yields of H₂, CO and hydrocarbon gases; (b) yield of CO₂.

can be seen that H₂ gas product followed the sequence of NaOH > KOH > Ca(OH)₂ > K₂CO₃ > Na₂CO₃ > NaHCO₃, indicating that the addition of NaOH under hydrothermal gasification generated the highest amount of H₂. Onwudili and Williams [17] reported that NaOH played two significant roles during hydrothermal biomass gasification. First, NaOH reacted with the biomass samples and degraded them to gasifiable intermediates. Second, during the gasification (water-gas shift) reaction, NaOH or sodium ions would capture carbon dioxide, thereby shifting this reaction equilibrium to forward direction. No CO and CO₂ were detected in the reaction with NaOH, however small trace of hydrocarbon gases was obtained. With respect to Fig. 1, it appears that all alkali catalysts used could partake in the biomass decomposition process but not possibly at different rates. Also, there were possible differences in their capability to promote the water-gas shift reaction. The catalytic effect of NaOH, KOH, Ca(OH)₂, Na₂CO₃, K₂CO₃ and NaHCO₃ is possibly attributed to the formation of formate salts such as sodium formate, potassium formate and calcium formate as intermediate in the reaction pathway to enhance the water-gas shift reaction. Hydrogen is obtained by the reaction between the formate salt with water [17,26].

A close examination of Fig. 1, shows that CO₂ was the major gaseous product obtained from hydrothermal conversion of glucose in the presence of NaHCO₃, Na₂CO₃, K₂CO₃, KOH and Ca(OH)₂, respectively. It was noticed that higher CO was detected when the experiment was carried out with Ca(OH)₂. Additionally, tar/oil was formed in the following order of NaHCO₃ > K₂CO₃ > Na₂CO₃ > KOH. Tar/oil formation is usually a consequence of dehydration and polymerization of biomass [17,34,35] and was observed in the presence of NaHCO₃, Na₂CO₃, K₂CO₃, KOH. The presence of tar/oil may indicate that NaHCO₃, Na₂CO₃, K₂CO₃ and KOH did not sufficiently decompose the glucose to the important gasifiable intermediates for H₂ production. Thus even with these alkaline compounds, dehydration and polymerization of glucose still occurred, whereas the addition of NaOH favoured the promotion of H₂ production through the gasification pathway.

Overall, the hydroxides gave higher H₂ gas than the carbonates as shown in Fig. 1(a). Although Ca(OH)₂ produced high H₂, it also produced the highest amount of CO and hydrocarbon gases compared with other catalysts. These observations highlight the implications of these catalysts on the predominant water-gas shift

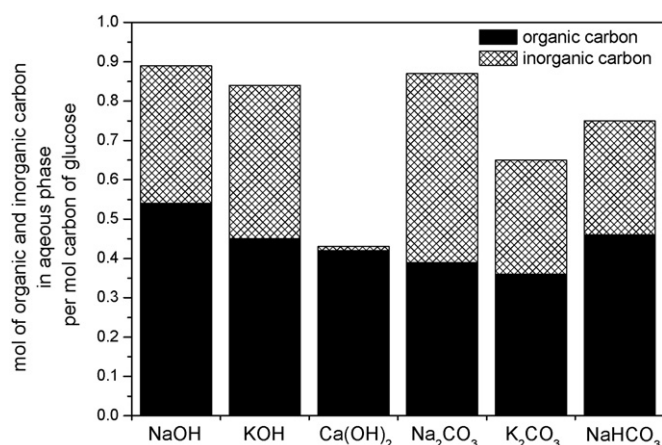


Fig. 2. Yields of TOC and TIC in aqueous phase obtained by sub-critical water gasification of glucose in the presence of 1.67 M NaOH.

chemistry operating during the gasification reactions. The hydroxide compounds had the ability of reacting with CO₂ to form metal carbonates. However, the bicarbonate and carbonates could not undergo this reaction of carbon oxide capture. The removal of the carbon oxides, in particular CO₂, was largely responsible for the increased production of H₂ gas, according to Le Chatelier's Principle [17]. Even if at all possible, the capture of carbon dioxide by the carbonates can only be a CO₂-exchange rather than a CO₂-removal process. This explains the predominance of CO₂ in the gas products when NaHCO₃, K₂CO₃ and Na₂CO₃ were used as catalysts. The high proportion of CO from Ca(OH)₂, may be linked to the low decomposition of calcium formate at 330 °C, leading to the unavailability of Ca²⁺ ions for CO₂ capture, which would have shifted the water-gas reaction to the right.

Additionally, the remaining carbon atoms from the glucose feed were found as inorganic and organic water-soluble products in the aqueous effluents. Fig. 2 illustrates the amount of total organic carbon product contained in aqueous phase. It was found that in the presence of NaOH, aqueous phase contained organic carbon about 163 mg out of a total organic carbon 303 mg in the feed glucose. It showed that slightly above half of the organic carbon was unconverted and remained in the liquid effluent. The liquid phase obtained in the presence of other catalysts; KOH, Ca(OH)₂, Na₂CO₃, K₂CO₃ and NaHCO₃ contained a lower amount of total organic carbon than that from NaOH. However, these catalysts produced lower H₂ yield as well as higher amount of carbon dioxide. This indicated that different reaction mechanisms were involved. Yu and Savage [36] have shown that decarboxylation and decarbonylation reactions are possible during hydrothermal biomass gasification. Consequently, decarbonylation appears to favour H₂ production via the water-gas-shift, especially if a CO₂ sorbent is available. Experimental results also show that the liquid effluent from the reaction involving Ca(OH)₂ contained the least inorganic carbon. The Ca(OH)₂ added could react with the dissolved CO₂ during the experiments and form insoluble CaCO₃ and thus precipitate out of solution, which was evidenced by the XRD results discussed later. Hence, the CO gas product and CaCO₃ product may have depleted the organic carbon contents of the aqueous effluents when Ca(OH)₂ was used.

The XRD scans of the solid residues obtained after evaporation of the liquid effluents are presented in Fig. 3. In case of NaOH, total water-soluble product contained sodium carbonate and sodium acetate as the main compounds. The detection of sodium acetate showed that acetic acid was formed during hydrothermal processing of biomass. Jin et al. [37] and Quitain et al. [38] studied hydrothermal conversion of biomass into acetic acid. Their results

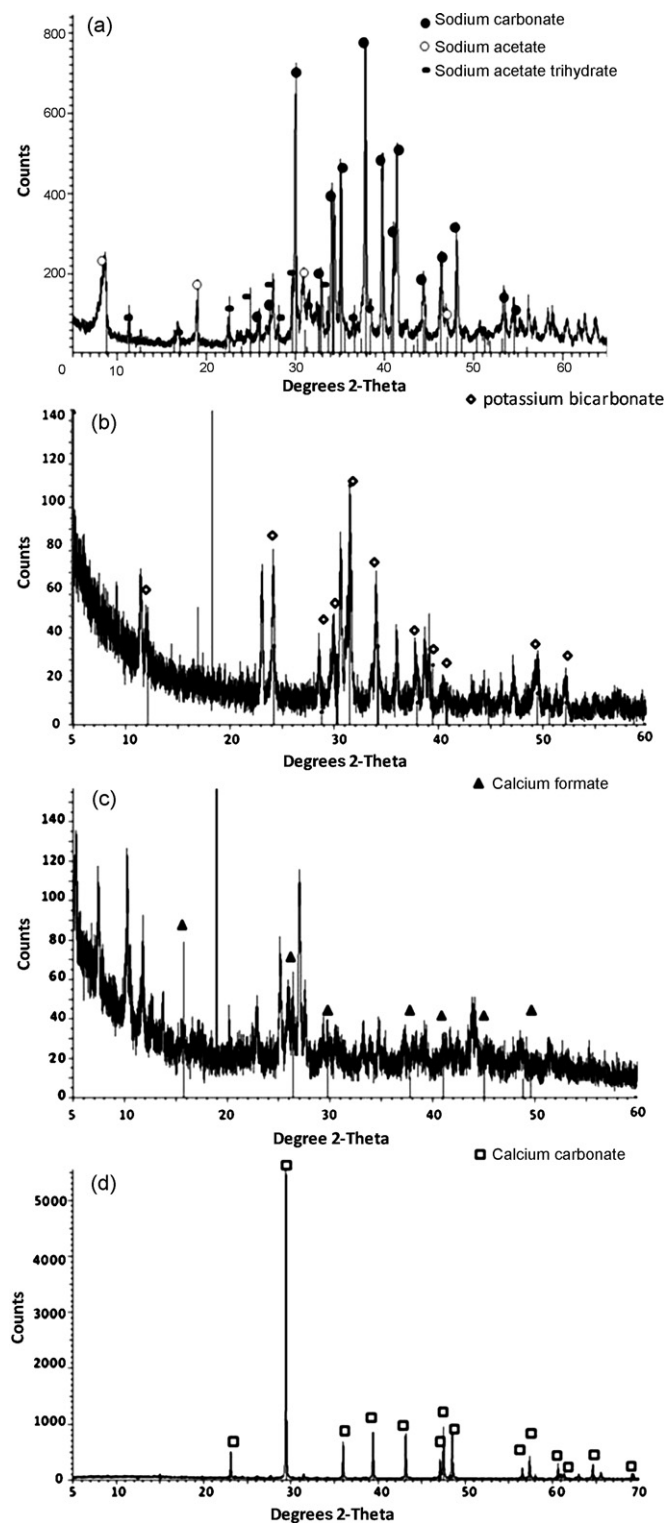


Fig. 3. XRD scans of dried water-soluble product and solid residue formed from sub-critical water gasification of glucose (a) NaOH; (b) KOH; (c)–(d) Ca(OH)₂.

showed that almost all food wastes or organic compounds could produce acetic acid as intermediate product under supercritical water oxidation. Jin and Enomoto [39], indicated that selected carbohydrate biomass such as glucose, cellulose, starch and rice hulls or various organic waste such as carrots, welsh onion, potato and beef suet could be converted to valuable chemicals such as acetic acid, formic acid and lactic acid. The addition of alkali catalysts has

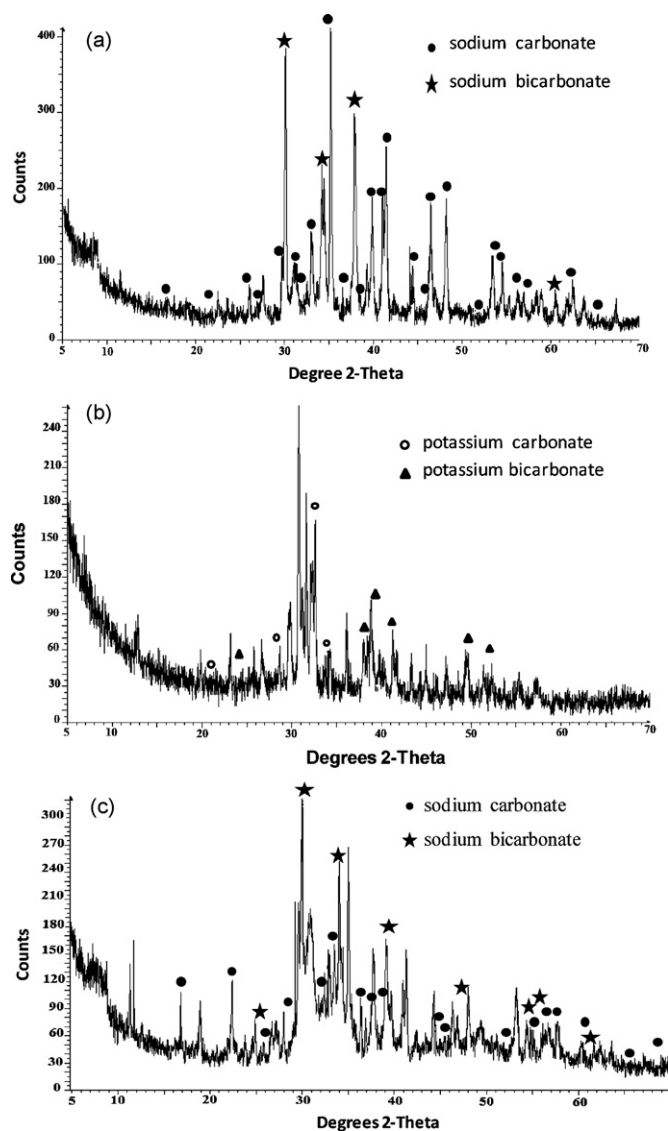


Fig. 4. XRD scans of dried water-soluble product and solid residue formed from sub-critical water gasification of glucose (a) Na_2CO_3 ; (b) K_2CO_3 ; (c) NaHCO_3 .

been reported to promote biomass conversion into these value-added products during hydrothermal oxidation experiments [39].

Meanwhile, potassium bicarbonate and calcium formate were major intermediate compounds in the XRD scans from residue s obtained in the presence of KOH and $\text{Ca}(\text{OH})_2$, respectively (Fig. 4). The presence of calcium formate confirmed that sub-critical water gasification of glucose/biomass could produce formic acid/formates as intermediate compounds. Formic acid is generally considered as a major intermediate product of hydrothermal decomposition of biomass and would exist as the metal salt in the presence of alkaline additives [37]. Onwudili and Williams [17] proposed a series of elementary reaction steps involving decarbonylation, water-gas shift reaction and CO_2 capture, in an attempt to explain the production of H_2 during alkali-promoted gasification of biomass. With the isolation of calcium formate crystals, this work thus confirmed formic acid formation under sub-critical water gasification with $\text{Ca}(\text{OH})_2$ catalyst. The presence of calcium formate in the liquid effluent showed that calcium formate was still stable under the hydrothermal conditions used in this work. On the other hand, sodium and potassium formates could be easily decomposed under these test conditions. Leyva et al. [40] reported that decomposition of pure $\text{Ca}(\text{COOH})_2$ should occur at around 470°C which is higher

Table 5

pH of liquid solutions before and after experiments in relation to the additives and biomass gasification after experiments at 330°C , 13.5 MPa and 120 min reaction time.

Additives	H_2O_2 (ER)	Catalyst (%w/v)	Before pH of liquid phase	After pH of liquid phase
NaOH	0.28	6.67	13.3	11.1
KOH	0.28	6.67	13.3	9.11
$\text{Ca}(\text{OH})_2$	0.28	6.67	11.4	6.67
Na_2CO_3	0.28	6.67	10.4	8.84
K_2CO_3	0.28	6.67	10.5	7.69
NaHCO_3	0.28	6.67	8.32	8.23

ER = oxidant equivalence ratio.

than 330°C used in this study. Moreover, only $\text{Ca}(\text{OH})_2$ produced an insoluble residue in this work, shown as calcium carbonate in the XRD scans.

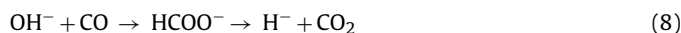
3.1.1. Discussion of ionic reactions in relation to the alkali catalysts

It is generally accepted that organic reactions in sub-critical water are ionic in nature [42]. It would appear that the production of H_2 during hydrothermal gasification of biomass with alkali additives may be linked to the basicity of the reaction medium. The basicity of reaction medium before and after running experiments presented by pH value of aqueous phase was shown in Table 5. Certainly, the hydroxide catalysts (NaOH , KOH and $\text{Ca}(\text{OH})_2$) were more basic than the carbonates and bicarbonates. On the other hand the basicity of the hydroxide additives is in the following order; $\text{NaOH} > \text{KOH} > \text{Ca}(\text{OH})_2$ and is similar to the trend in H_2 production. One possible mechanism for this observation is the continuous regeneration of basicity throughout the duration of the hydrothermal reaction. Kruse et al. [20] and Penninger and Rep [41] have reported that the formation of formate intermediate results from the reaction between OH^- and CO . The decomposition of the formate by reacting with water produces H_2 and carbonate ion. Thus, depending on the solubility of carbonate, it could react with water to produce more OH^- that would then react with CO in a cyclic process until no CO is available in the medium. The formation and decomposition of the formate salt would depend therefore on the basicity of the medium.

The presence of NaOH , KOH and $\text{Ca}(\text{OH})_2$, being more highly basic in aqueous solutions, could have increased the basicity of the medium than the carbonates or bicarbonates. This would in turn promote H_2 production due to a higher possibility of formation of formate salt. The difference in H_2 production between these hydroxide additives may be linked to the different levels of basicity they contribute to the medium as well as the availability of the carbonate ions in solution. For instance, sodium and potassium formates can be easily decomposed at 330°C and release their metal ions to the reaction medium. The metal ions would react with CO_2 from the water-gas shift reaction and form soluble carbonates. However, calcium formate did not completely decompose under the test condition according to XRD scans. Even when decomposed, the reaction of calcium ions with CO_2 to form insoluble calcium carbonate. This would render the carbonate ions unavailable to generate OH^- ions, which would react with CO . This may explain why CO was prevalent in the gas products when $\text{Ca}(\text{OH})_2$ was used.

Lower H_2 production from the carbonate and bicarbonate additives may indicate the inability of these additives to promote the water-gas shift reaction in the forward direction. Na_2CO_3 and NaHCO_3 gave different gas products. Na_2CO_3 generated higher H_2 and lower CO_2 than NaHCO_3 . Under sub-critical water conditions carbonate anion could react with water to form bicarbonate and OH^- reacting with CO to form the formate anion [41]. The formate

ion could further decompose into CO_2 and hydride anion according to the reaction equation:



The H^- obtained from Eq. (9) further interacts with water leading to H_2 and OH^- formation, according

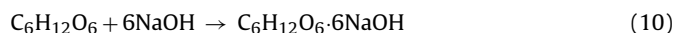


The formation of H_2 could increase when the reaction Eq. (8) is accelerated and shifted towards the right hand side. There are two possible methods to do this. Firstly, increasing the basicity of water as the reaction medium by providing extra OH^- anions and secondly by the removal of CO_2 . From these reasons, the hydroxide catalysts would be more useful in providing more hydroxide ions and also for CO_2 removal. For example, NaOH , KOH and Ca(OH)_2 could not only raise OH^- but also reduce CO_2 gas by capturing CO_2 to form sodium/potassium/calcium carbonate or sodium/potassium bicarbonate. Na_2CO_3 and K_2CO_3 would dissociate into CO_3^{2-} reacting with H_2O to create extra OH^- anions and HCO_3^- while NaHCO_3 could dissociate into HCO_3^{2-} and Na^+ cation. However, Na_2CO_3 , K_2CO_3 and NaHCO_3 are slightly more acid (or less basic) with low dissociation constant leading to lower OH^- formation [34,41,42]. Frantz [43] reported that K_2CO_3 has a relative low dissociation constant leading to low basicity in water. From this reason, it could be inferred that OH^- concentration from carbonated alkali catalyst should be lower than that from NaOH or KOH . For HCO_3^- anion, it has higher stability than CO_3^{2-} thus the reaction shown in Eq. (7) can be shifted towards the right hand side. Moreover, the salts of bi-valent cations are much more acidic or less basic than the corresponding alkali salts of mono-valent cations. Hence, NaOH and KOH can be said to have higher basicity than Ca(OH)_2 [34].

Based on the work of Onwudili and Williams [17], Kruse et al. [14,34,44], Penninger et al. [41] and Frantz [43] the predominant reaction equations for sub-critical water gasification experiments using these six alkali additives and hydrogen peroxide are thought to be as follows:

For NaOH , KOH and Ca(OH)_2 , the reaction equations would be identical, so we have shown only equations using NaOH

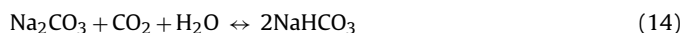
Partial oxidation



Water-gas shift reaction



CO_2 -capture reaction for NaOH , KOH and Ca(OH)_2 :



For additives, Na_2CO_3 and K_2CO_3 , we have also used Na_2CO_3 to show the possible reaction equations as follows:



Hydrogen is then obtained by the reaction of the formate with water

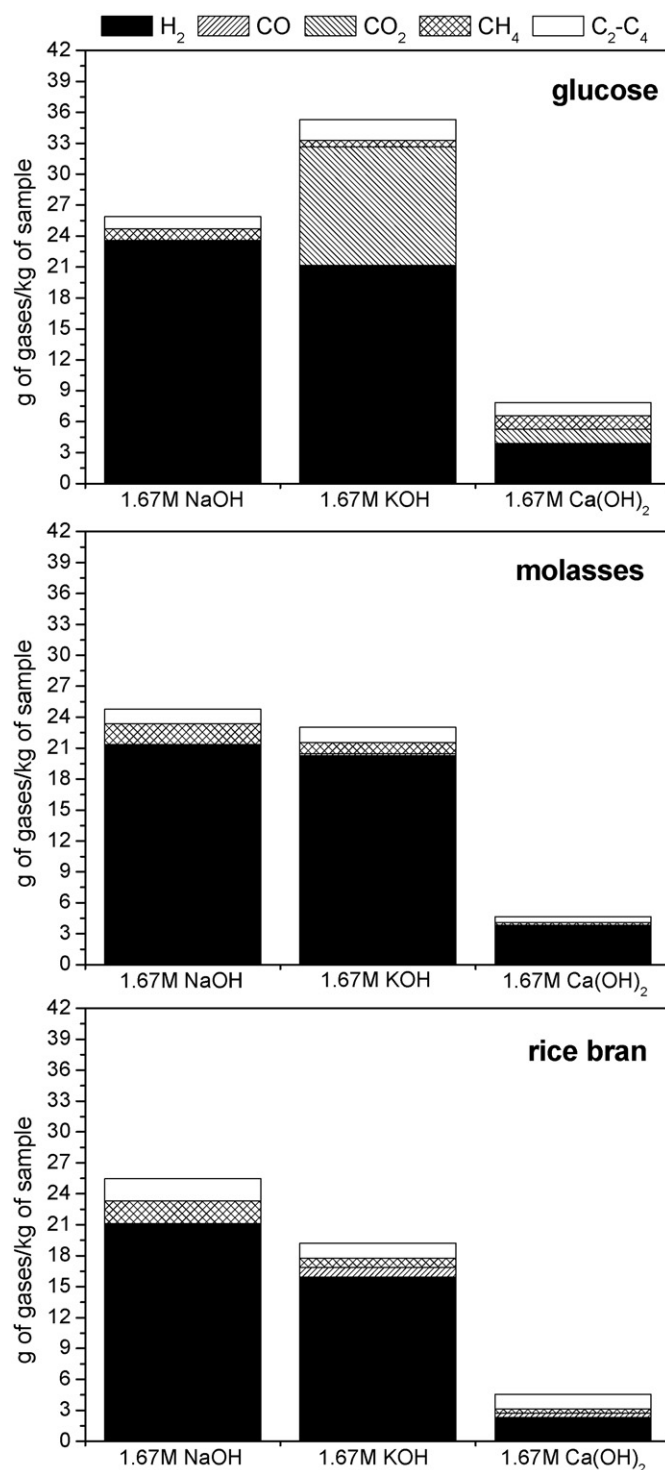
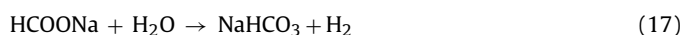


Fig. 5. Gaseous products from sub-critical water gasification of glucose, molasses and rice bran in the presence of 1.67 M each of NaOH , KOH and Ca(OH)_2 .

Note that Eq. (17) can again be explained by the water-gas shift reaction.

For additive, NaHCO_3 ;

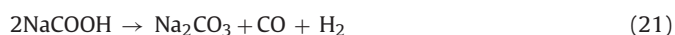
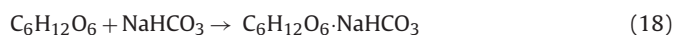
NaHCO_3 gave an enhanced H_2 formation and with low yield of CO and may be due to hydrogen production in two steps as illustrated below:

Table 6

Overall mass balance of products obtained from the gasification of 0.75 g of real food processing waste with 1 g of each alkali catalyst (NaOH, KOH, Ca(OH)₂) at reaction temperature of 330 °C and reaction time of 60 min.

Sample	Catalysts (1.67 M)	H ₂ (mg)	CO (mg)	CO ₂ (mg)	CH ₄ (mg)	C ₂ –C ₄ (mg)	Solid residues (mg)	Tar/oil (mg)	TWSP (mg)	H ₂ O (mg)	% mass balance
Glucose	NaOH	17.7	–	–	0.80	6.01	–	–	1470	438	97.4
Molasses	NaOH	9.91	–	–	1.20	1.20	–	–	1370	416	82.4
Rice bran	NaOH	15.3	–	–	1.61	1.72	100	–	1500	395	102
Glucose	KOH	14.1	–	7.60	0.43	1.31	–	–	1820	370	93.1
Molasses	KOH	15.2	0.10	–	0.80	1.12	20.0	–	1570	370	84.1
Rice bran	KOH	12.0	0.71	–	0.70	1.11	20.0	–	1820	336	83.4
Glucose	Ca(OH) ₂	2.90	–	1.00	1.00	1.02	1810	–	252	580	93.7
Molasses	Ca(OH) ₂	2.82	0.10	–	0.20	0.41	1660	–	377	583	92.8
Rice bran	Ca(OH) ₂	1.81	0.30	–	0.30	1.31	1490	–	294	590	84.4

Partial oxidation reaction:



Once CO is produced, water-gas shift reaction could occur as shown in Eq. (12).

However, each of these additives could react with acetic acid, another major intermediate product of biomass oxidation, forming the acetate salts of the corresponding metals [31,39]. Results showed that in the presence of NaHCO₃, H₂ formation increased while CO formation declined. Sue and Arai [45] reported that the dissociation of KOH and other hydroxides showed a very low dependence on temperature in the sub-critical region and decrease very much at the critical point of water. NaOH, KOH and Ca(OH)₂ have predominant reaction to capture CO₂ to form CO₃²⁻ salts leading to an increased reaction rate of the water-gas shift reaction forward towards higher H₂ production. This observation may indicate that the CO₂-capture reaction was superior to OH⁻ generation from any of the additives. In a nutshell, all the additives could generate different concentrations of OH⁻ ions in sub-critical water which was useful in the decomposition of biomass samples. Results show that higher OH⁻ concentration conferred higher basicity to the reaction medium and thus higher chance for the formation of gasifiable intermediates through carbon–water reaction. Moreover, the promotion of water-gas shift via CO₂ removal may be a more significant process during hydrothermal biomass gasification. It is therefore clear that the hydroxide additive would be better suited for promoting H₂ production via the water-gas shift reaction.

3.2. Hydrothermal gasification of food processing wastes with hydroxide additive

Since the hydroxide catalysts (NaOH, KOH and Ca(OH)₂) gave better results in terms of H₂ production from glucose, the experimental conditions were replicated for real food processing waste including molasses and rice bran. The experiments were carried out with 1 g of each of the additives and 0.75 g of the food waste materials.

The variation of the gas products with addition of these three additives is shown in Fig. 5. Generally, NaOH produced the highest H₂ yield compared to KOH and Ca(OH)₂. The yield of H₂ was fairly similar, irrespective of the feedstock. This could be as a result of the identical elemental compositions of the feeds in term of carbon, hydrogen and oxygen, indicating that they were all carbohydrate-type biomasses. The effectiveness of NaOH to decompose this type of biomass and catalyze the subsequent water-gas shift reaction is well known [17,26,34].

Moreover, it is interesting to see that the effect of each additive on the different biomass samples was essentially similar. For both KOH and Ca(OH)₂, significant yields of CO₂ were observed from the three different samples, while the yields of H₂ gas were lower than with NaOH. This was much lower in the case of Ca(OH)₂. Hence, the catalytic performance of NaOH was superior to that of KOH and Ca(OH)₂, in H₂ production from the different samples. The effect of Ca(OH)₂ may be linked to the unavailability of calcium ions to catalyze the water-gas shift reaction by being tied up as calcium formate, as discussed earlier. Again Ca(OH)₂, produced more solid residues than NaOH and KOH due to the formation of insoluble calcium carbonate.

Table 6 presents the product mass balances obtained during hydrothermal gasification of glucose, molasses and rice in the presences of NaOH, KOH and Ca(OH)₂ catalysts. The results show that oil/tar was not found during this sub-critical water gasification of glucose, molasses and rice bran in the presence of any of the additives. Rice bran was slightly more resistant to degradation than glucose and molasses within the test conditions when compared with glucose and molasses. This may be due to rice bran comprising of hemi-cellulose and oil, which may be difficult to decompose under sub-critical water conditions. In summary, NaOH, KOH and Ca(OH)₂, additives reacted with glucose, molasses and rice bran to produce mainly, H₂ under sub-critical water without tar/oil and char formation but with different degrees of effectiveness.

4. Conclusions

Hydrothermal gasification by partial oxidation of glucose was carried out with various alkali catalysts; NaOH, KOH, Ca(OH)₂, Na₂CO₃, K₂CO₃, NaHCO₃. The results show that H₂ yield in relation to the alkaline additives was in the following order; NaOH > KOH > Ca(OH)₂ > K₂CO₃ > Na₂CO₃ > NaHCO₃. The H₂ yield indicated that hydroxides of alkali metal catalyst are more effective for the production of H₂ during sub-critical water gasification than carbonates and bicarbonate alkaline additives. The primary driving force for alkaline hydrothermal gasification may be the strength of the basicity of the medium, which preferentially caused the decomposition of biomass into gasifiable intermediates. Catalysts of the hydroxide ion group, NaOH, KOH and Ca(OH)₂, were selected to react with glucose, molasses and rice bran under hydrothermal condition set at a mild temperature of 330 °C for 60 min of reaction time. The results indicated that NaOH, KOH and Ca(OH)₂ could promote biomass decomposition and improve the amount of H₂ product via the water-gas shift reaction. In addition, NaOH, KOH and Ca(OH)₂ inhibited and suppressed tar and char formation. It was found that NaOH generated the highest amount of H₂ due to enhancement of the water-gas shift reaction by intermediate formation of formate salts. No CO or CO₂ was detected because NaOH could capture CO₂, thereby shifting this reaction equilibrium in the

forward direction. Meanwhile small traces of hydrocarbon gases were obtained, comprised of mainly methane gas. Consequently, carbohydrate-like by-products/wastes from the food processing industry such as molasses and rice bran could be used as renewable resources for hydrothermal production of hydrogen gas at relatively low temperature in the presence of alkali metals catalysts.

Acknowledgements

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